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חוק הפטנטים, התשכ"ז-1967
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בקשה לפטנט
Application for Patent

אני, (שם המבקש, מענו – ולגבי גוף מאוגד – מקום התאגדותו)
I (Name and address of applicant, and, in case of a body corporate, place of incorporation)

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(בעברית) (Hebrew) קתודות של בריום-מנגן עבור מצברים אלקליים

(באנגלית) (English) BARIUM MANGANESE SALT CATHODES FOR ALKALINE BATTERIES

מבקש בזאת כי ינתן לי עליה פטנט.
hereby apply for a patent to be granted to me in respect thereof.

• בקשת חלוקה – Application for Division	• בקשת פטנט מוסף – Application for Patent of Addition	• דרישת דין קדימה Priority Claim		
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No. ____ מס'	No. ____ מס'			
dated ____ מיום	dated ____ מיום			

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P.O.A.: general / specific – attached / to be filed later –
Has been filed in case ____ הוגש בענין

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BARIUM MANGANESE SALT CATHODES FOR ALKALINE BATTERIES

The present invention relates to electric storage batteries. More particularly, the invention relates to a novel alkaline electric storage battery with a cathode formed from a barium manganese compound.

BACKGROUND OF THE INVENTION

MnO_2 is the common active cathode material in primary alkaline batteries. As an alternative to MnO_2, a variety of permanganate compounds have been considered for cathode materials due to their high oxidation state which, in principle permits significant storage and release of electrical charge. However, as described by J. Epstein and C. C. Liang, U. S. Patent, 3,799,959 (Oct. 12, 1971), most permanganates salts are overly soluble in alkaline solution and this solubility can be destructive to the battery performance. In addition, most permanganate salts do not discharge effectively in the solid phase, although as described by S. Licht and C. Marsh, United States Patent 5,549,991, (Aug. 27, 1996), in the solution phase they can support high currents.

Compared to the manganese dioxide alkaline cathode reaction, both manganates and permanganates can have a significantly higher faradaic capacity and higher cathodic potential. The thermodynamic potential for the $1e^-$ permanganate to manganate reduction in aqueous alkaline media is:

$$MnO_4^- + 1e^- \rightarrow MnO_4^{2-} \qquad E = 0.56V \text{ vs SHE} \qquad (1)$$

and manganate also can exhibit a direct discharge to manganese dioxide, summarized as the $2e^-$ reduction:

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^- \quad E = 0.58V \text{ vs SHE} \tag{2}$$

and alternately permanganate also can exhibit a direct discharge to manganese dioxide, summarized as the 3e$^-$ reduction:

$$MnO_4^{2-} + 2H_2O + 2e^- \rightarrow MnO_2 + 4OH^- \quad E = 0.58V \text{ vs SHE} \tag{3}$$

In addition, the MnO_2 product can undergo a further 1e- reduction, as utilized in the conventional commercial alkaline (Zn anode / MnO_2 cathode) cell:

$$2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^- \quad E = 0.35V \text{ vs SHE} \tag{4}$$

Manganate salts, being in the less oxidized manganese valence state of Mn(VI), will store less charge in principle, than the permanganates. This lower valence state would also suggest that they would be considered to be less chemically active. In principal, as described by equations 2 and 4, permanganate salts can undergo a total of a 4e$^-$ alkaline cathodic reduction, and by equations 3 and 4 manganate salts can undergo a total of a 3e$^-$ alkaline cathodic reduction. Yet the manganate and permanganate salts have not replaced the widely used commercial alkaline MnO2 cathode due to a general perception that these salts are too soluble (creating a tendency to react and decompose the anode), and that they exhibit only inefficient, and/or low current density, charge transfer.

It is an object of the present invention to provide an additive to the cathode in alkaline batteries which provides a practical storage capacity greater than the theoretical capacity known for these cathode materials. A novel electrochemically active solid cathode is

demonstrated using barium manganate. The standard electrochemical potentials for manganate and MnO_2 electrochemical reduction in alkaline solution are well known.

BRIEF DESCRIPTION OF THE INVENTION:

The invention relates to an electrical storage cell, so-called alkaline battery, comprising two half-cells which are in electrochemical contact with one another through an electrically neutral alkaline ionic conductor, wherein one of said half-cells comprises an anode and the other half-cell comprises a cathode, whereby electrical storage is accomplished via electrochemical reduction of the cathode and oxidation of the anode. The cathode contains an electrochemically active barium manganate or barium permanganate compound.

BRIEF DESCRIPTION OF THE FIGURES:

Figure 1 is a diagrammatic illustration of the fluorinated, polymer graphite containing cathode battery according to the invention; and

Figures 2 to 5: illustrate graphically performance of various battery aspects according to the invention as described in the Examples.

DETAILED DESCRIPTION OF THE INVENTION

The novel battery according to the present invention is based on the addition of an electrochemically active barium manganate material

or barium permanganate material to form a cathode in an alkaline battery.

The phrase "theoretical charge capacity " refers to the calculated charge capacity of that cathode material in accord with the known number of faradays (moles electrons) stored per mole of that material. The theoretical charge capacity is calculated through equation 5 and where n is the number of discharge electrons, F is the Faraday's constant = 26.801 Amp hour per mol, and Fw is the formula weight:

$$\text{Theoretical charge capacity} = n \times F / Fw \qquad (5)$$

For any specified known cathode material, discharged at low current density rate, the phrase "conventional cathode storage capacity" is specifically the theoretical charge capacity of that cathode material. At higher rates of current density, this "conventional cathode storage capacity" is less than the theoretical charge capacity, and refers to the maximum amount of cathode storage capacity previously attainable for the cathode material at this discharge condition. Table 1 presents the theoretical storage capacity of various cathode materials calculated in accord with equation 2, 3 and 4.

The anode of the battery may be selected from the known list of metals capable of being oxidized, typical such as zinc, cadmium, lead, iron, aluminum, lithium, magnesium, calcium; and other metals such as copper, cobalt, nickel, chromium, gallium, titanium, indium, manganese, silver, cadmium, barium, tungsten, molybdenum, sodium, potassium, rubidium and cesium.

The anode may also be of other typical constituents capable of being oxidized, examples include, but are not limited to hydrogen,

(including but not limited to metal hydrides), inorganic salts, and organic compounds including aromatic and non-aromatic compounds. The anode may also be of other typical constituents used for lithium-ion anodic storage, examples include, but are not limited to lithium-ion in carbon based materials and metal oxides.

Table 1 - Theoretical charge capacity of several known cathode materials, determined with equation 2

cathode material	cathode name	n	Fw kg/mole	Charge capacity Amp hour/kg
MnO_2	manganese dioxide	1	86.9	308
NiOOH	nickel oxyhydroxide	1	91.7	289
Ag_2O	silver oxide	2	231.7	231
HgO	mercury oxide	2	216.6	247
$BaMnO_4$	barium manganate	3	256.3	314
$Ba(MnO_4)_2$	barium permanganate	8	375.2	571

The electrically neutral alkaline ionic conductor utilized in the battery according to the present invention, comprises a medium that can support current density during battery discharge in an alkaline medium. A typical representative ionic conductor is an aqueous solution preferably containing a high concentration of a hydroxide such as KOH. In other typical embodiments, the electrically neutral ionic conductor comprises a high concentration of NaOH.

An electric storage battery according to the invention may be rechargeable by application of a voltage in excess of the voltage as measured without resistive load, of the discharged or partially discharged cell.

According to another embodiment of the invention, means are provided to impede transfer of chemically reactive species, or prevent electric contract between the anode and cathode. Said means includes, but is not limited to a non-conductive separator configured with open channels, a membrane, a ceramic frit, grids or pores or agar solution; such means being so positioned as to separate said half cells from each other.

DETAILED DESCRIPTION OF FIGURE 1

Figure 1 illustrates schematically an electrochemical cell 10 based on a cathode which contains a barium manganese compound half cell, an electrically neutral alkaline ionic conductor and an anode. The cell contains an electrically neutral alkaline ionic conductor 22, such as a concentrated aqueous solution of KOH, in contact with a cathode which contains a fluorinate, polymer graphite 14. Reduction of the cathode, is achieved via electrons available from the electrode 14. The anode electrode 12, such as in the form of metal is also in contact with the electrically neutral ionic conductor 22. Electrons are released in the oxidation of the anode. Optionally, the cell may contain a separator 20, for minimizing the non-electrochemical interaction between the cathode and the anode.

The invention will be hereafter illustrated in further detail with reference to the following non-limiting examples, it being understood that the Examples are presented only for a better understanding of the invention without implying any limitation thereof, the invention

being covered by the claims. Although the examples used AAA cells, it will be appreciated by those skilled in the art that the increase in performance may be obtained regardless of the cell size. It will be understood by those who practice the invention and by those skilled in the art, that various modifications and improvements may be made to the invention without departing from the spirit of the disclosed concept.

Example 1

Salts which are less soluble are preferred as cathodic materials. An experiment was carried out, the object being to demonstrate the low solubility of barium manganate in potassium hydroxide solutions of concentrations similar to those used in alkaline batteries. As measured in Figure 2, the solubility of barium manganate is low compared to that of other permanganate and manganate salts. In the storage cell, low solubility, or insolubility is preferred to minimize parasitic cathode/anode interactions. The lighter alkali permanganate salts have a high aqueous solubility, e.g. 4 **m** (**m** ≡ molal) for $LiMnO_4$, and 0.5 **m** for $KMnO_4$, whereas the respective solubility of 0.07 **m** and 0.01 **m** for $RbMnO_4$ and $CsMnO_4$ is very low. Whereas the solubility of the alkali earth magnesium, calcium, strontium and barium permanganates, is very high (e.g.. 9, 8 and 2 **m** respectively for $Ca(MnO_4)_2$, $Sr(MnO_4)_2$ and $Ba(MnO_4)_2$), the solubility of barium manganate, $BaMnO_4$, is very low.

Example 2

An experiment was carried out, the object being to demonstrate that the barium manganate, prepared as a cathode mix under the same conditions as the common permanganate salt, $KMnO_4$, discharges to a substantially higher fraction of it's theoretical cathodic charge. Salts

that can discharge to a higher percentage of their theoretical cathodic charge, are preferred as alkaline cathodic salts.

Cells are prepared with identical zinc anodes and separators, as removed from commercial AAA alkaline cells. Cell potential and energy capacity of alkaline super-iron AAA cells were measured during discharge at a constant load rate of 75 Ω. Cells contain either 3.5 g $KMnO_4$, or 4.1 g $BaMnO_4$ in the 9 weight percent graphite mix, and 9 weight percent 13.5 molar KOH electrolyte. The Percent Storage Capacity is determined by the measured cumulative ampere hours, compared to the theoretical capacity. Under these conditions, and as seen in the figure middle, a cathode comprised of only $KMnO_4$, exhibits less than half of the capacity of the $BaFeO_4$ cathode. Figure 3, shows that barium manganate, prepared as a cathode mix under the same conditions as the common permanganate salts, $KMnO_4$, discharges to a substantially higher fraction of it's theoretical cathodic charge.

A cathode which discharges to a high total energy, is preferred. Figure 4, presents the higher discharge energy measured for the barium manganate cathode, compared to a $KMnO_4$ cathode under the same conditions. The figure summarizes the measured discharge of NaMnO4, or $KMnO_4$ compared to the $BaMnO_4$ cathode alkaline AAA cells. Despite the lower intrinsic Mn(VI $\rightarrow$IV) capacity of the barium manganate salt, this salt's cathode approaches 1.0 Wh, yielding a higher discharge capacity than the sodium or potassium permanganate cathode cells. As is evident in the figure, the measured discharge capacity is higher, despite the lower intrinsic $4e^-$ capacities, for the heavier alkali cation permanganates compared to the lighter alkali permanganates. The measured capacity of sodium, and potassium permanganate

cathodes is ~0.45 Wh and 0.8 Wh. The sodium permanganate discharge required a higher fraction (32 weight percent) of graphite to generate a discharge.

Example 3

An experiment was carried out, the object being to demonstrate that a $BaMnO_4$ mixed with the common MnO_2 alkaline cathode, can improve the MnO_2 discharge performance. A material which can be mixed with the common MnO_2 alkaline cathode, thereby improving the MnO_2 discharge performance, is preferred over the MnO_2 cathode by itself. Figure 5, shows a MnO_2 cathode prepared mixed with $BaMnO_4$, exhibits a higher discharge energy, than that of the MnO_2 cathode alone.

Example 4

In a alternate configuration $Ba(MnO_4)_2$ can also be used as an alkaline cathode. In accord with the high solubility summarized in Figure 2, $Ba(MnO_4)_2$ would not normally considered as a viable cathode for an alkaline battery. However, we have found that $Ba(MnO_4)_2$, prepared as a mix of $KMnO_4$ and $Ba(OH)_2$, exhibits little solubility in a concentrated KOH solution or a KOH solution with added $Ba(OH)_2$. This provides an attractive material as a cathode in this electrolyte.

CLAIMS:

1. A battery comprising two half-cells which are in an electrochemical contact with one another through an electrically neutral alkaline ionic conductor, wherein one of said half-cells comprises an anode and the other half-cell comprises a cathode, whereby electrical discharge is accomplished via reduction of the cathode and oxidation of the anode, and whereby said cathode includes at least 1% of weight of barium manganate.

2. A battery comprising two half-cells which are in an electrochemical contact with one another through an electrically neutral alkaline ionic conductor, wherein one of said half-cells comprises an anode and the other half-cell comprises a cathode, whereby electrical discharge is accomplished via reduction of the cathode and oxidation of the anode, and whereby said cathode includes at least 5% of weight of barium manganate.

3. A battery comprising two half-cells which are in an electrochemical contact with one another through an electrically neutral alkaline ionic conductor, wherein one of said half-cells comprises an anode and the other half-cell comprises a cathode, whereby electrical discharge is accomplished via reduction of the cathode and oxidation of the anode, and whereby said cathode includes at least 25% of weight of barium manganate.

4. A battery comprising two half-cells which are in an electrochemical contact with one another through an electrically neutral alkaline ionic conductor, wherein one of said half-cells comprises an anode and the other half-cell comprises a cathode, whereby electrical discharge is accomplished via reduction of the cathode and oxidation of the anode, and whereby said cathode includes at least 1% of weight of barium permanganate.

5. A battery comprising two half-cells which are in an electrochemical contact with one another through an electrically neutral alkaline ionic conductor, wherein one of said half-cells comprises an anode and the other half-cell comprises a cathode, whereby electrical discharge is accomplished via reduction of the cathode and oxidation of the anode, and whereby said cathode includes at least 5% of weight of barium permanganate.

6. A battery comprising two half-cells which are in an electrochemical contact with one another through an electrically neutral alkaline ionic conductor, wherein one of said half-cells comprises an anode and the other half-cell comprises a cathode, whereby electrical discharge is accomplished via reduction of the cathode and oxidation of the anode, and whereby said cathode includes at least 25% of weight of barium permanganate.

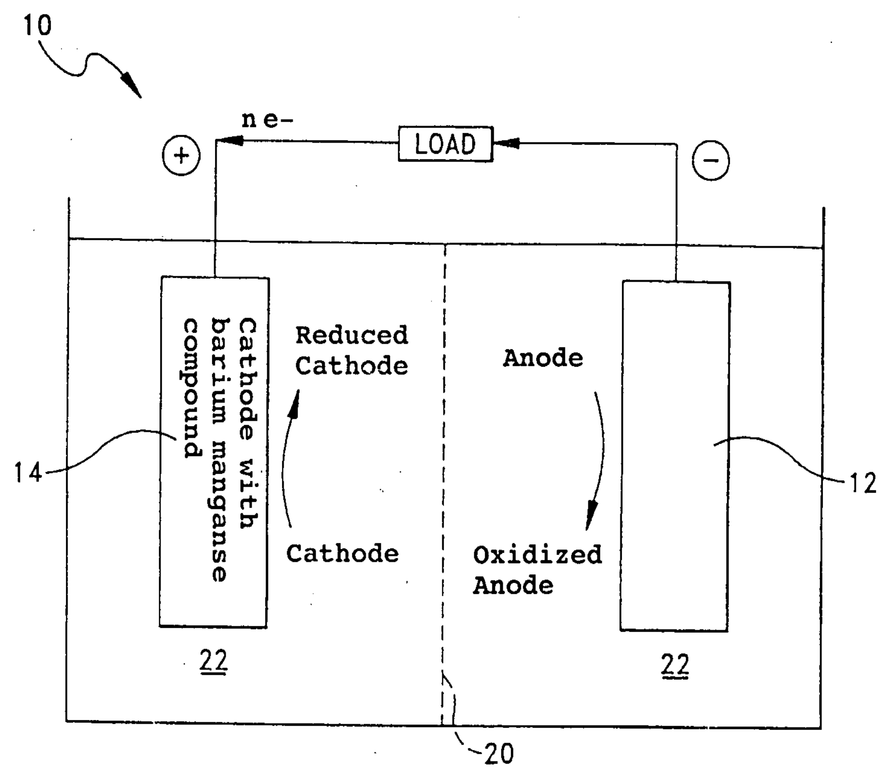
10
ne-
LOAD
+
−
Cathode with barium manganse compound
Reduced Cathode
Cathode
Anode
Oxidized Anode
14
12
22
22
20

FIG. 1

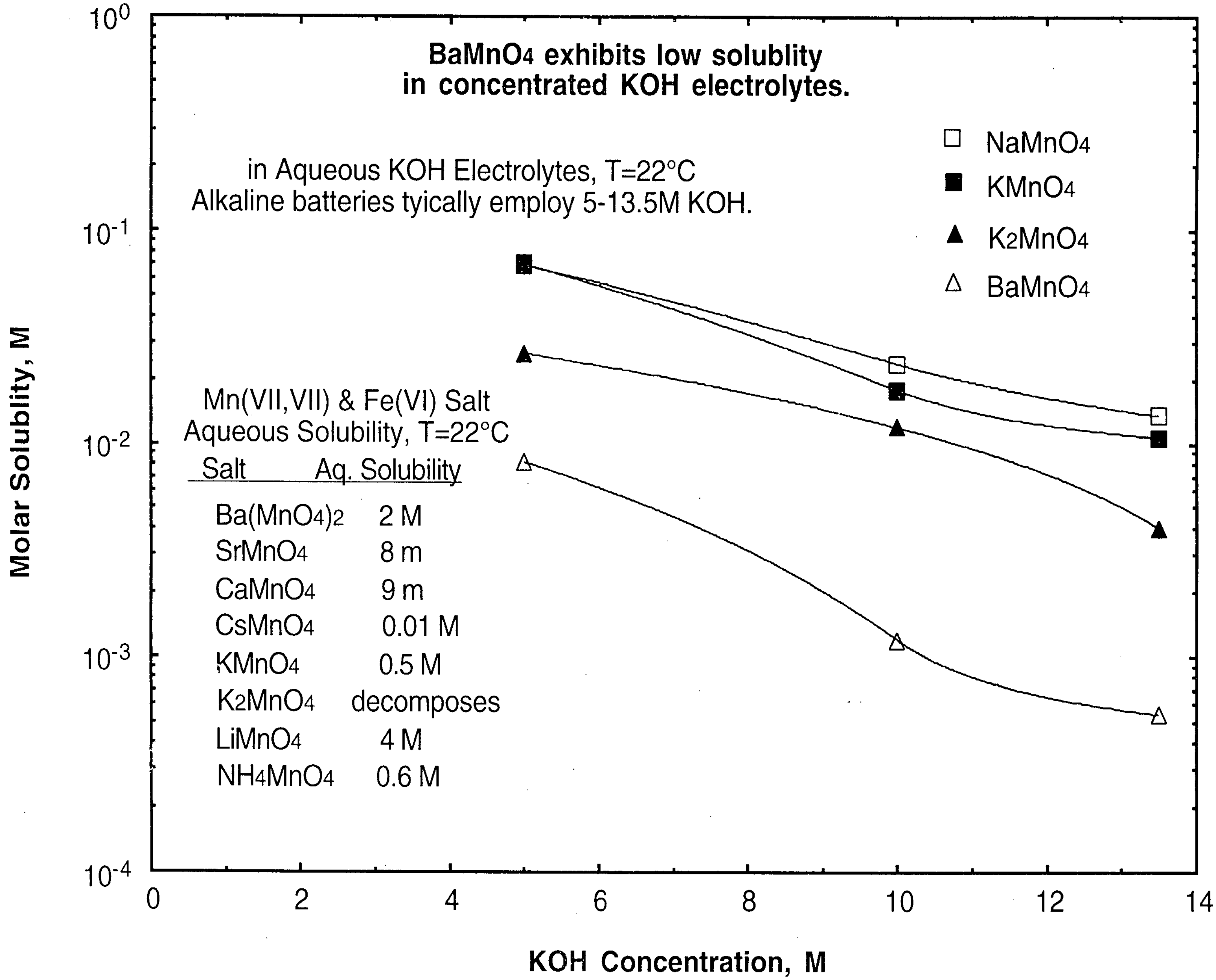
BaMnO4 exhibits low solublity
in concentrated KOH electrolytes.
in Aqueous KOH Electrolytes, T=22°C
Alkaline batteries tyically employ 5-13.5M KOH.
NaMnO4
KMnO4
K2MnO4
BaMnO4
Mn(VII,VII) & Fe(VI) Salt
Aqueous Solubility, T=22°C
Salt Aq. Solubility
Ba(MnO4)2 2 M
SrMnO4 8 m
CaMnO4 9 m
CsMnO4 0.01 M
KMnO4 0.5 M
K2MnO4 decomposes
LiMnO4 4 M
NH4MnO4 0.6 M
Molar Solublity, M
10^0
10^-1
10^-2
10^-3
10^-4
0
2
4
6
8
10
12
14
KOH Concentration, M

Figure 2

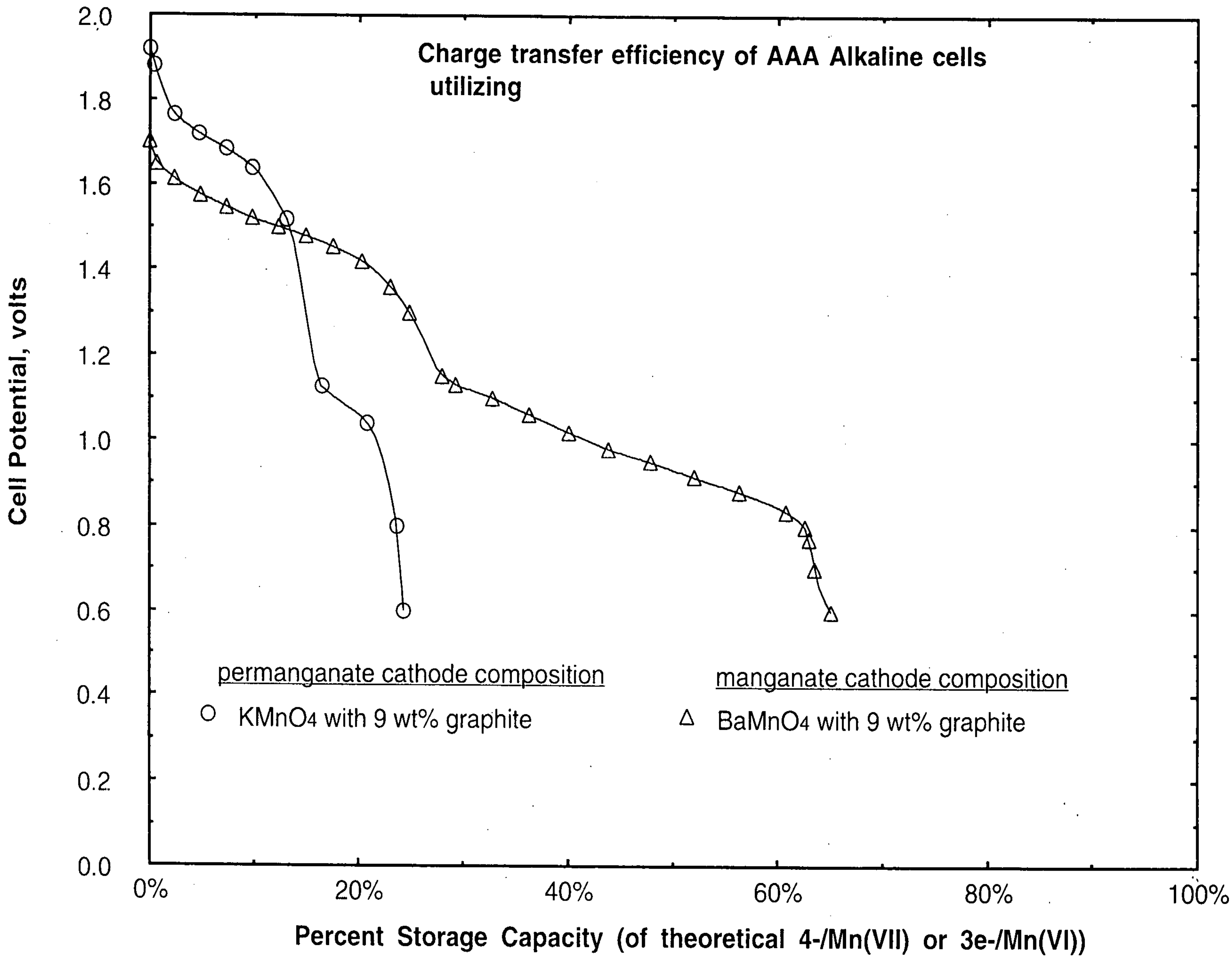
Charge transfer efficiency of AAA Alkaline cells utilizing
Cell Potential, volts
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0%
20%
40%
60%
80%
100%
Percent Storage Capacity (of theoretical 4-/Mn(VII) or 3e-/Mn(VI))
permanganate cathode composition
○ KMnO4 with 9 wt% graphite
manganate cathode composition
△ BaMnO4 with 9 wt% graphite

Figure 3

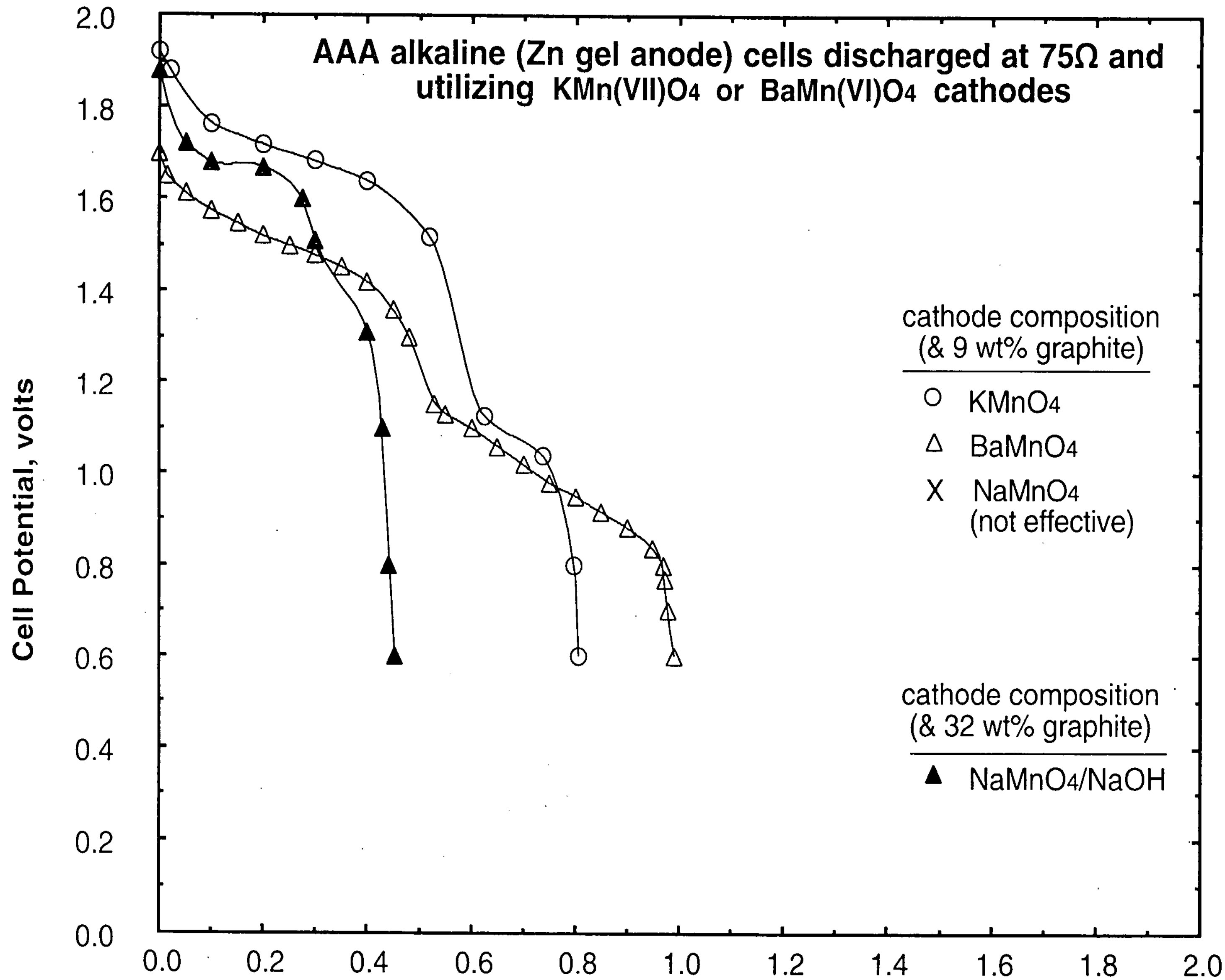
AAA alkaline (Zn gel anode) cells discharged at 75Ω and utilizing KMn(VII)O4 or BaMn(VI)O4 cathodes
Cell Potential, volts
Discharge Energy, Wh
cathode composition (& 9 wt% graphite)
KMnO4
BaMnO4
NaMnO4 (not effective)
cathode composition (& 32 wt% graphite)
NaMnO4/NaOH
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0

Figure 4

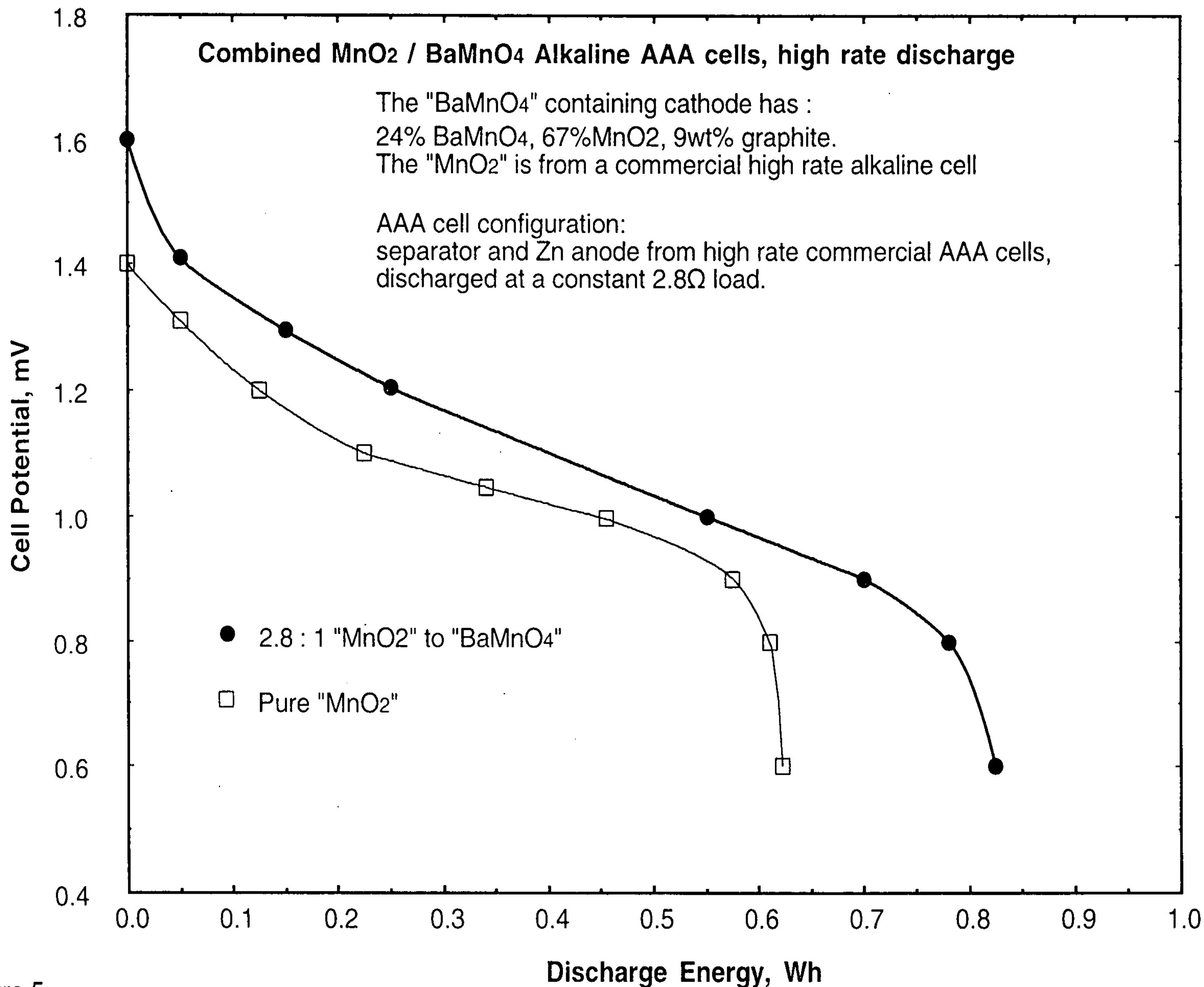
Combined MnO2 / BaMnO4 Alkaline AAA cells, high rate discharge
The "BaMnO4" containing cathode has :
24% BaMnO4, 67%MnO2, 9wt% graphite.
The "MnO2" is from a commercial high rate alkaline cell
AAA cell configuration:
separator and Zn anode from high rate commercial AAA cells,
discharged at a constant 2.8Ω load.
2.8 : 1 "MnO2" to "BaMnO4"
Pure "MnO2"
Cell Potential, mV
Discharge Energy, Wh
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

Figure 5